



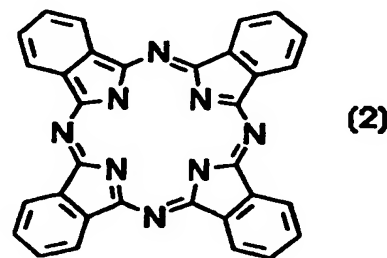
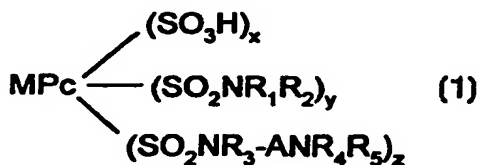
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C09B 47/26, C09D 11/00</b>	<b>A1</b>	(11) International Publication Number: <b>WO 98/49240</b> (43) International Publication Date: 5 November 1998 (05.11.98)
(21) International Application Number: PCT/GB98/01015 (22) International Filing Date: 6 April 1998 (06.04.98) (30) Priority Data: 9708533.6                      26 April 1997 (26.04.97)                      GB (71) Applicant (for all designated States except US): ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): CARR, Kathryn [GB/GB]; Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB). (74) Agents: KIRK, Martin, John; Zeneca Specialties, Intellectual Property Group, P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB) et al.		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report.

(54) Title: PHTHALOCYANINE INK-JET DYES

## (57) Abstract

Phthalocyanine compounds of formula (1) and all IJP-effective forms of such compounds have utility as colorants in inks for ink-jet printing; in said formula, M represents a metal or H; Pc represents a phthalocyanine nucleus of formula (2);  $x + y + z$



represents an average from 3 to 4; and  $z$  may be zero; A represents  $\text{C}_{1-4}$ -alkylene;  $\text{R}_1, \text{R}_3$  each independently represent H or  $\text{C}_{1-4}$ -alkyl;  $\text{R}_4$  represents H; or  $\text{C}_{1-4}$ -alkyl optionally substituted with hydroxy;  $\text{R}_5$  represents a carboxylic acid substituted aryl group; and  $\text{R}_2$  represents H,  $\text{C}_{1-4}$ -alkyl or a group of formula BD where: B represents  $\text{C}_{1-4}$ -alkylene; and D represents  $\text{NR}_6\text{R}_7$ ; or  $\text{SC}_{1-4}\text{alkyleneSO}_3\text{H}$ ; where:  $\text{R}_6$  represents H; or  $\text{C}_{1-4}$ -alkyl, optionally substituted by hydroxy;  $\text{R}_7$  represents H;  $\text{C}_{1-4}$ -alkyl, optionally substituted by hydroxy or morpholino; or  $\text{R}_6$  and  $\text{R}_7$  together with the N atom to which they are attached form a morpholino or piperazino ring.

BEST AVAILABLE COPY

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

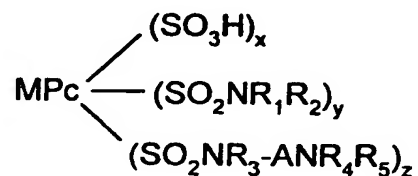
PHTHALOCYANINE INK-JET DYES

This invention relates to compounds, to ink compositions comprising them and to the use of such inks in ink jet printing ("IJP"). IJP is a non-impact printing technique in which droplets of ink are ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

5 There are many demanding performance requirements for colorants and inks used in IJP. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks  
10 should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle.

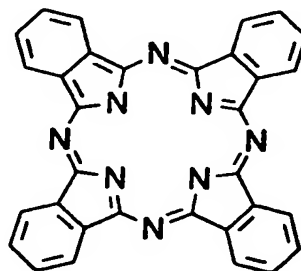
The applicant has discovered that certain phthalocyanine compounds have particular utility as colorants for use in IJP as they may produce prints with unexpectedly good optical density, light fastness and/or water fastness.

15 According to the present invention there is provided a compound of Formula (1):\*



Formula (1)

20 which includes all IJP-effective forms of such compounds; and in which  
M represents a metal or H;  
Pc represents a phthalocyanine nucleus of Formula (2)



25  $x + y + z$  represents an average from 3 to 4; and  $z$  may be zero.  
A represents  $\text{C}_{1-4}$ -alkylene;  
 $\text{R}_1, \text{R}_3$  each independently represent H or  $\text{C}_{1-4}$ -alkyl;

$R_4$  represents H; or  $C_{1-4}$ -alkyl optionally substituted with hydroxy;

$R_5$  represents a carboxylic acid substituted aryl group; and

$R_2$  represents H,  $C_{1-4}$ -alkyl or a group of formula BD

where

5 B represents  $C_{1-4}$ -alkylene; and

D represents  $NR_6R_7$ ; or  $SC_{1-4}$ alkylene $SO_3H$ ;

where

$R_6$  represents H; or  $C_{1-4}$ alkyl, optionally substituted by hydroxy;

10  $R_7$  represents H;  $C_{1-4}$ alkyl, optionally substituted by hydroxy or morpholino;  
or  $R_6$  and  $R_7$  together with the N atom to which they are attached form a  
morpholino or piperazino ring.

When M is a metal it is preferably selected from Li, Na, K, Mg, Ca, Ba, Al, Si, Sn, Pb, Rh, Sc, Ti, V, Cr, Mn, Fe, Co, Ni and Cu, more preferably from Sc, Ti, Va, Cr, Mn, Fe, Co, Zn, Ni and Cu and especially from Ni and Cu.

15 Preferred dyes of Formula (1) are either those dyes in which:

$R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are H; A is  $-CH_2CH_2-$ ; and  $R_5$  is carboxylic acid substituted phenyl, more preferably 3-carboxyphenyl; or

those dyes in which:

20 M is Cu, z is 0,  $R_1$  is H,  $R_2$  is BD where B is  $-CH_2CH_2-$  and D is  $NR_6R_7$ , more preferably  
 $NHCH_2CH_2OH$ .

It is preferred that  $(x+y)>z$  and/or  $x>y$ . More preferably either: x is an average of about 3.0 and y is an average of about 1.0 and z is zero; or x is an average of about 1.3, y is an average of about 1.2 and z is an average of about 1.5.

25 Any radical group mentioned herein as a substituent refers to a monovalent radical  
unless otherwise stated. A group which comprises a chain of three or more atoms  
signifies a group in which the chain may be straight or branched or the chain or part of the  
chain may form a ring. For example, an alkyl group may comprise: propyl which includes  
n-propyl and isopropyl; butyl which includes n-butyl, sec-butyl, isobutyl and tert-butyl; and  
an alkyl group of three or more carbon atoms may comprise a cycloalkyl group. The total  
30 number of certain atoms is specified herein for certain substituents, for example  $C_{1-n}$ alkyl,  
signifies an alkyl group having from 1 to 'n' carbon atoms. The term 'halo' as used herein  
signifies fluoro, chloro, bromo and iodo radicals.

35 The term 'IJP effective' (for example with reference to the inks, compositions,  
ingredients, substituents and/or compounds described herein) will be understood to mean  
effective for use in ink-jet printing by for example: providing desirable properties to the ink,  
being compatible with any inert carriers and/or diluents suitable for formulating such inks,  
being compatible with ink jet printers and/or capable of being ink-jet printed. In relation to  
the processes described herein effective compounds are those which will undergo the

specified reactions to form the compounds of the present invention. To be particularly acceptable for use in IJP compounds of Formula (1) may be Ames negative.

IJP-effective forms of compounds of Formula(1) may be selected from one or more of the following (including mixtures thereof and combinations thereof in the same molecular moiety): salts, stereoisomers, zwitterions, polymorphic forms, complexes and isotopically substituted forms. Specific compounds of Formula (1) comprise those compounds exemplified herein; all IJP-effective salts thereof, preferably their potassium, sodium or ammonium salts; and IJP-effective mixtures thereof.

Compounds of Formula (1) may be in the form as shown in the structures herein (i.e. free acid form) but are preferably in the form of salts. Salts of Formula (1) may be formed from one or more organic and/or inorganic bases and/or acids and compounds of Formula (1) which are acidic and/or basic (for example acid and/or base addition salts). Salts of Formula (1) comprise all IJP-effective salts that may be formed from monovalent and/or multivalent acids and/or bases. Salts of Formula (1) also comprise all enantiomeric salts formed with IJP-effective chiral acids and/or bases and/or any mixtures of enantiomers of such salts (for example racemic mixtures). The dyes may be converted into a salt using known techniques. The present invention comprises all IJP-effective salts of Formula (1) and IJP-effective mixtures thereof.

Preferred salts of Formulae (1) are alkali metal salts (especially lithium, sodium and potassium salts), and optionally substituted ammonium salts (especially salts with ammonia and volatile amines). More preferred salts are those with a cation of formula  $^+NT_4$  where each T is independently H or optionally substituted alkyl, or two groups represented by T are H or optionally substituted alkyl and the remaining two groups represented by T, together with the N atom to which they are attached, form a 5 or 6 membered ring (preferably a morpholine, pyridine or piperidine ring). Most preferably each T is independently H or  $C_{1-4}$ alkyl, especially H,  $CH_3$  or  $CH_3CH_2$ , more especially H. Examples of cations which are IJP-effective comprise:  $^+NH_4$ , morpholinium, piperidinium, pyridinium,  $(CH_3)_3N^+H$ ,  $(CH_3)_2N^+H_2$ ,  $H_2N^+(CH_3)(CH_2CH_3)$ ,  $CH_3N^+H_3$ ,  $CH_3CH_2N^+H_3$ ,  $H_2N^+(CH_2CH_3)_2$ ,  $CH_3CH_2CH_2N^+H_3$ ,  $CH_3CH_2CH_2N^+H_3$ ,  $(CH_3)_2CHN^+H_3$ ,  $N^+(CH_3)_4$ ,  $N^+(CH_2CH_3)_4$ , N-methyl pyridinium, N,N-dimethyl piperidinium and N,N-dimethyl morpholinium.

Certain compounds of Formula (1) may exist as one or more stereoisomers, for example, enantiomers, diastereoisomers, geometric isomers, tautomers, conformers and/or combinations thereof within the same moiety. The present invention comprises all IJP-effective stereoisomers of compounds of Formula (1) and IJP-effective mixtures thereof.

Certain compounds of Formula (1) may exist as one or more zwitterions, for example, moieties which comprise two or more centres of ionic charge. The present

invention comprises all IJP-effective zwitterions of Formula (1) and IJP-effective mixtures thereof.

Certain compounds of Formula (1) may exist as one or more polymorphs, for example, phases, crystalline forms, amorphous forms, solid solutions, interstitial compounds and/or any mixtures thereof. The present invention comprises all IJP-effective polymorphs of Formula (1) and IJP-effective mixtures thereof.

Certain compounds of Formula (1) may exist in the form of one or more other complexes in addition to the metal complexes shown herein, for example, chelates, solvates, other organometallic complexes, and/or complexes with other IJP-effective ligands. Such complexes may be formed between an suitable substrate in which the compound of Formula (1) and/or the substrate may act as a ligand. The substrate may comprise one or more solvents to form solvates. The complexes may be non-stoichiometric, for example if the complex is a hydrate it may comprise a hemihydrate, monohydrate and/or dihydrate. The present invention comprises all IJP-effective complexes of Formula (1) and IJP-effective mixtures thereof.

Certain compounds of Formula (1) may exist as one or more isotopic forms in which one or more atoms in Formula (1) comprise one or more isotopes. The natural ratios of various isotopes may be altered by suitable means, for example certain  $^{12}\text{C}$  atoms in certain compounds of Formula (1) may be substantially replaced by the less common  $^{14}\text{C}$  and/or  $^{13}\text{C}$  isotopes. Optionally certain isotopic forms of Formula (1) may be radio-active. Certain of the isotopic forms of Formula (1) may be used as means for selective imaging in imaging devices (for example devices using X-rays, positron emission tomography and/or nuclear magnetic resonance); and/or as tools to investigate the mode of action of compounds of Formula (1) in IJP. The present invention comprises all IJP-effective, isotopic forms of Formula (1) and IJP-effective mixtures thereof.

The present invention relates to all compounds of Formula (1) even those which may not be directly effective for use in IJP because they exhibit undesirable properties. Such compounds may nevertheless have utility in the field of the present invention for example as intermediates in the preparation and/or purification of IJP-effective compounds of Formula (1) and/or as research tools and/or diagnostic aids in relation to IJP.

Compounds of Formula (1) may be prepared the methods described below and by other suitable methods analogous to those described in the art for similar phthalocyanine compounds.

A preferred method for preparing dyes of Formula (1) comprises the following steps:

a) Preparing a compound of formula  $\text{MPc}(\text{SO}_2\text{Cl})_{x+y+z}$  using methods known per se. A preferred method preparing a compound of formula  $\text{MPc}(\text{SO}_2\text{Cl})_{x+y+z}$  comprises heating (preferably for about 1 to about 24 hours), a metal-free or metal containing

phthalocyanine (optionally comprising one to four sulpho groups) with chlorosulphonic acid, preferably at a temperature above about 60°C, more preferably above about 100°C, most preferably from about 120°C to about 165°C. Optionally this may be followed by heating (preferably for about 10 to about 48 hours, more preferably for about 10 to about 30 hours), the phthalocyanine with  $\text{PCl}_3$ , preferably at lower temperature than with the chlorosulphonic acid, more preferably from about 80°C to about 105°C.

- b) Condensing the compound of formula  $\text{MPc}(\text{SO}_2\text{Cl})_{x+y+z}$  in water at 0°C with a halo amine of formula  $\text{NHR}_3\text{AX}$ , where X is halo, preferably chloro. More preferably the haloamine is in the form of its hydrochloride salt.
- c) Treating the halogenated adduct from step b) with ammonium hydroxide and warming the reaction mixture to 40°C for about 1 hour.
- d) Reacting the material from step c) with an amine of formula  $\text{NHR}_4\text{R}_5$  in aqueous solution at about 70°C for about 3 hours to produce a dye of Formula (1).

Alternatively to prepare certain compounds of the invention, steps c) and d) above may be replaced by step c1):

c1) Reacting the material from step b) with an amine of formula  $\text{NHR}_2\text{R}_3$  or a thiol of formula  $\text{HSC}_{1-4}\text{alkyleneSO}_3\text{H}$ , in aqueous solution at about 70°C for about 3 hours to produce a dye of Formula (1).

The reactions leading to the formation of the present compounds may be performed under conditions that have been described in the art and compounds of Formula (1) may be isolated by known methods such as spray drying or precipitation followed by filtration.

Preferably the ink of the present invention comprises:

- (a) from 0.01 to 30 parts of an IJP-effective compound of Formula (1); and
- (b) from 70 to 99.99 parts of a liquid medium or a low melting point solid medium; wherein all parts are by weight and the number of parts of (a)+(b)=100.

The number of parts of component (a) is preferably from 0.1 to 20, more preferably from 0.5 to 15, and especially from 1 to 5 parts. The number of parts of component (b) is preferably from 99.9 to 80, more preferably from 99.5 to 85, especially from 99 to 95 parts.

When the medium is a liquid, preferably component (a) is completely dissolved in component (b). Preferably component (a) has a solubility in component (b) at 20°C of at least 10%. This allows the preparation of concentrates which may be used to prepare more dilute inks and reduces the chance of the colorant precipitating if evaporation of the liquid medium occurs during storage.

Preferred liquid media include water, a mixture of water and an organic solvent and an organic solvent free from water.

When the medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50 and especially from 95:5 to 80:20. Preferably the organic solvent comprising the

mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents. The liquid medium may comprise water and preferably two or more, more preferably from 2 to 8, water-soluble organic solvents.

Preferred water-miscible organic solvents comprise:

- 5  $C_{1-6}$ -alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and/or cyclohexanol;  
linear amides, preferably dimethylformamide and/or dimethylacetamide;  
ketones and/or ketone-alcohols, preferably acetone, methyl ether ketone, cyclohexanone and/or diacetone alcohol;
- 10 water-miscible ethers, preferably tetrahydrofuran and/or dioxane;  
diols, preferably  $C_{2-12}$ diols (for example pentane-1,5-diol, ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and/or thiodiglycol) and/or oligo- and/or poly-alkyleneglycols (for example diethylene glycol, triethylene glycol, polyethylene glycol and/or polypropylene glycol);
- 15 triols, preferably glycerol and/or 1,2,6-hexanetriol;  
 $C_{1-4}$ alkyl ethers of diols, preferably mono $C_{1-4}$ alkyl ethers of  $C_{2-12}$ diols: {for example 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy)ethoxy]-ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and/or ethyleneglycol monoalkyl ether};
- 20 cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and/or 1,3-dimethylimidazolidone;  
cyclic esters, preferably caprolactone;  
sulphoxides, preferably dimethyl sulphoxide and/or sulpholane; and/or  
all IJP-effective mixtures thereof.

- 25 More preferred water-soluble organic solvents are selected from:  
cyclic amides (e.g. 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone);  
diols, (e.g. 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol);  
 $C_{1-4}$ alkyl ethers of diols (e.g. 2-methoxy-2-ethoxy-2-ethoxyethanol); and
- 30 all IJP-effective mixtures thereof.

A preferred liquid medium comprises:

- (a) from 75 to 95 parts water; and
  - (b) from 25 to 5 parts in total of one or more solvents selected from:  
diethylene glycol, 2-pyrrolidone, thiodiglycol, N-methylpyrrolidone, cyclohexanol,
  - 35 caprolactone, caprolactam and pentane-1,5-diol;
- where the parts are by weight and the sum of the parts (a) + (b) = 100.

Another preferred liquid medium comprises:

- (a) from 60 to 80 parts water;
- (b) from 2 to 20 parts diethylene glycol; and



(c) from 0.5 to 20 parts in total of one or more solvents selected from:

2-pyrrolidone, N-methylpyrrolidone, cyclohexanol, caprolactone, caprolactam, pentane-1,5-diol and thiodiglycol;

where the parts are by weight and the sum of the parts (a) + (b) + (c) = 100.

5           Examples of further IJP-effective media for inks of the present invention comprise a mixture of water and one or more organic solvents are described in US 4,963,189, US 4,703,113, US 4,626,284 and EP 0425150-A.

10           When the liquid medium comprises an organic solvent free from water, (i.e. less than 1% water by weight) the solvent preferably has a boiling point of from 30° to 200°C, more preferably of from 40° to 150°C, especially from 50 to 125°C. The organic solvent may be water-immiscible, water-miscible or a mixture of such solvents. Preferred water-miscible organic solvents comprise any of those described above and mixtures thereof. Preferred water-immiscible solvents comprise aliphatic hydrocarbons; esters (for example ethyl acetate) chlorinated hydrocarbons (for example dichloromethane), ethers  
15 (for example diethyl ether) and mixtures thereof.

          When the liquid medium comprises a water-immiscible organic solvent, preferably it comprises a polar solvent (for example a C<sub>1-4</sub>alkanol) to enhance the solubility of the dye in the liquid medium. It is especially preferred that where the liquid medium is an organic solvent free from water it comprises a ketone (especially methyl ethyl ketone)  
20 and/or an alcohol (especially a C<sub>1-4</sub>alkanol, more especially ethanol or propanol).

          The organic solvent free from water may be a single organic solvent or a mixture of two or more organic solvents. It is preferred that when the medium is an organic solvent free from water it is a mixture of 2 to 5 different organic solvents. This allows a medium to be selected which gives good control over the drying characteristics and  
25 storage stability of the ink.

          Ink media comprising an organic solvent free from water are particularly useful where fast drying times are required and particularly when printing onto hydrophobic and non-absorbent substrates, for example plastics, metal and glass.

          Preferred low melting solid media have a melting point in the range from 60°C to  
30 125°C. Suitable low melting point solids include long chain fatty acids or alcohols, preferably those with C<sub>18-24</sub>chains, and sulphonamides. The dye of Formula (1) may be dissolved in the low melting point solid or may be finely dispersed in it.

          The ink may also contain additional components conventionally used in inks for IJP, for example viscosity and surface tension modifiers, corrosion inhibitors, biocides,  
35 kagation reducing additives and surfactants which may be ionic or non-ionic.

          A further aspect of the invention provides a process for printing an image on a substrate comprising applying to the substrate by means of an ink jet printer, an ink of the present invention as defined herein.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small orifice onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the orifice, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the orifice. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the orifice.

The substrate is preferably paper, plastic, a textile, metal or glass, more preferably paper, an overhead projector slide or a textile material, especially paper. Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character.

A further aspect of the present invention provides a paper, an overhead projector slide or a textile material printed with an ink and/or a colorant as defined herein and/or by means of a process as defined herein.

When the substrate is a textile material the ink according to the invention is preferably applied thereto by:

- i) applying the ink to the textile material using an ink jet printer; and
- ii) heating the printed textile material at a suitable temperature, preferably from 50°C to 250°C, to fix the ink on the material.

Preferred textile materials are natural, synthetic and semi-synthetic materials. Examples of preferred natural textile materials include wool, silk, hair and cellulosic materials, particularly cotton, jute, hemp, flax and linen. Examples of preferred synthetic and semi-synthetic materials include polyamides, polyesters, polyacrylonitriles and polyurethanes.

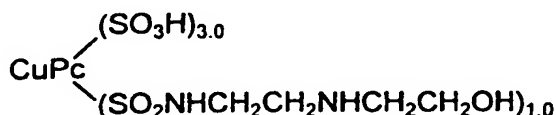
Preferably the textile material has been treated with an aqueous pre-treatment composition comprising a thickening agent and optionally a water-soluble base and a hydrotropic agent and dried prior to step i) above.

The pre-treatment composition preferably comprises a solution of the base and the hydrotropic agent in water containing the thickening agent. Particularly preferred pre-treatment compositions are described more fully in EP 0534660-A.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

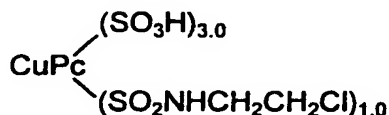
#### Example 1

Preparation of



a) Preparation of  $\text{CuPc}(\text{SO}_2\text{Cl})_4$ 

Copper phthalocyanine (115g) was added in portions to stirred chlorosulphonic acid (308 ml) over 30 minutes keeping the temperature below 50°C. The mixture was stirred for 30 minutes before being heated gradually to 140°C, at which temperature it was stirred for 3 hours. The mixture was cooled to 40°C and phosphorus trichloride (52.5g) was added in portions over 30 minutes, whilst the temperature was kept below 50°C. The mixture was stirred overnight at room temperature and then cooled to 0°C and poured onto a mixture of ice (700g), water (700g), concentrated hydrochloric acid (40 ml) and sodium chloride (100g). The mixture was stirred at 0°C for 30 minutes. The precipitated product was collected by filtration at reduced pressure and washed with ice-cold hydrochloric acid solution (0.5 M, 1.5 l) to obtain a paste of  $\text{CuPc}(\text{SO}_2\text{Cl})_4$ .

b) Reaction with b-chloroethylammonium chloride to obtain:

15

A solution of b-chloroethylammonium chloride (34.7 g) in water (1 l) was cooled to 0°C and the sulphonyl chloride paste from step a) was added. The pH of the mixture was adjusted to 7 to 8 with dilute sodium hydroxide solution. The mixture was stirred at 0°C for 1 hour, heated to 40°C and stirred at that temperature for a further hour and then cooled to room temperature. The pH of the mixture was adjusted to 1.5 with concentrated hydrochloric acid and the mixture was stirred for 1 hour. The precipitated product was collected by filtration at reduced pressure and washed with dilute hydrochloric acid solution (0.5 M, 1.5 l) to obtain the above chloro compound.

20

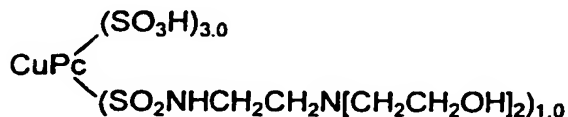
c) Reaction with ethanolamine to produce Example 1

A solution of the chloro compound from step b) (38g) and ethanolamine (25g) in water (350 ml) was stirred at 70°C for 4 hours. Sodium chloride (25% w/v) was added to the warm mixture and the stirring was continued for a further 30 minutes. The mixture was allowed to cool and the resultant precipitate was collected by filtration at reduced pressure and washed with cold brine (75 ml) and dried to produce the title dye.

30

Example 2

Preparation of



35

Steps a) and b) are carried out as Example 1 above.

c) Reaction with diethanolamine to produce Example 2

A solution of the chloro compound from step b) (38g) and diethanolamine (42g) in water (350 ml) was stirred at 70°C for 4 hours. The product was then isolated as described above in Example 1 step c) to produce the title dye.

Example 3

Preparation of



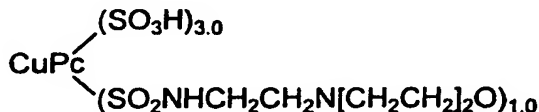
Steps a) and b) are carried out as Example 1 above.

c) Reaction with 4-(2-aminoethyl)morpholine to produce Example 3

A solution of the chloro compound from step b) (38g) and 4-(2-aminoethyl)morpholine (52g) in water (350 ml) was stirred at 70°C for 4 hours. The product was then isolated as described above in Example 1 step c) to produce the title dye.

Example 4

Preparation of



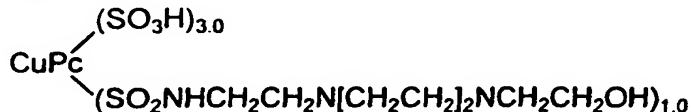
Steps a) and b) are carried out as Example 1 above.

c) Reaction with morpholine to produce Example 4

A solution of the chloro compound from step b) (38g) and morpholine (35g) in water (350 ml) was stirred at 70°C for 4 hours. The product was then isolated as described above in Example 1 step c) to produce the title dye.

Example 5

Preparation of



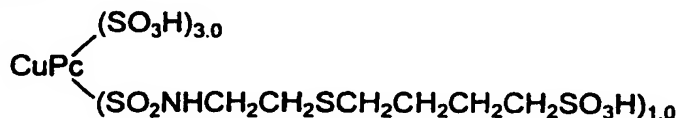
Steps a) and b) are carried out as Example 1 above.

c) Reaction with 1-(2-hydroxyethyl)piperazine to produce Example 5

A solution of the chloro compound from step b) (38g) and 1-(2-hydroxyethyl)piperazine (47 ml) in water (350 ml) was stirred at 70°C for 4 hours. The product was then isolated as described above in Example 1 step c) to produce the title dye.

Example 6

Preparation of



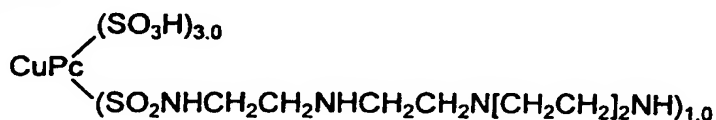
Steps a) and b) are carried out as Example 1 above.

c) Reaction with 3-mercaptopropane sulphonic acid to produce Example 6

A solution of the chloro compound from step b) (35g) and the sodium salt of 3-mercaptopropane sulphonic acid (26g) in water (350 ml) was stirred at 50°C and pH 9 for 7 hours. The product was then isolated as described above in Example 1 step c) [with the modification that the pH of the mixture after adding sodium chloride was adjusted to 1.0 with concentrated hydrochloric acid] to produce the title dye.

Example 7

Preparation of



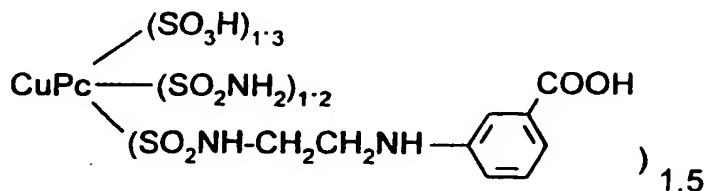
Steps a) and b) are carried out as Example 1 above.

c) Reaction with 1-(2-aminoethyl)piperazine to produce Example 7

A solution of the chloro compound from step b) (38g) and 1-(2-aminoethyl)piperazine (52 ml) in water (350 ml) was stirred at 70°C for 4 hours. The product was then isolated as described above in Example 1 step c) to produce the title dye.

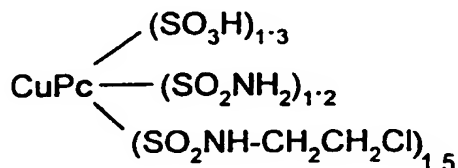
Example 8

Preparation of



Step a) is carried out as Example 1 above.

b) Reaction with b-chloroethylammonium chloride to obtain:



5

A solution of b-chloroethylammonium chloride (34.7 g) in water (1 l) was cooled to 0°C and the sulphonyl chloride paste from step a) was added. The pH of the mixture was adjusted to 7 to 8 with dilute ammonium hydroxide solution. The mixture was stirred at 0°C for 1 hour, heated to 40°C and stirred at that temperature for a further hour and then cooled to room temperature. The pH of the mixture was adjusted to 1.5 with concentrated hydrochloric acid and the mixture was stirred for 1 hour. The precipitated product was collected by filtration at reduced pressure and washed with dilute hydrochloric acid solution (0.5 M, 1.5 l) to obtain the above chloro compound.

10

15

c) Reaction with 3-aminobenzoic acid to produce Example 8

A solution of the chloro compound from step b) (50g) and 3-aminobenzoic acid (35g) in water (300 ml) at pH 7.0 was heated to 70°C and stirred at that temperature for 4 hours. Sodium chloride (25% w/v) was added and the pH of the mixture was adjusted to 6.0 with concentrated hydrochloric acid. The resultant precipitate was collected by filtration at reduced pressure and washed with acid brine (25%, 100 ml, pH 4) and methanol (100 ml) to obtain as the product the title dye.

20

### Salts

The exemplified sodium salts (examples 1 to 8) prepared as described above, may be used after suitable purification directly in ink formulations as described below or may be converted to other IJP-effective salts as follows. Each example was dissolved in distilled water. The solution was filtered and the volume of the filtrate adjusted to 4 litres. The solution was desalinated by reverse osmosis. The dissolved sodium salt may be converted into other salt [e.g. the potassium salt] by passing the solution through an ion-exchange column comprising Dowex HGRW resin saturated with a suitable solution [e.g. potassium hydroxide solution (5% w/v)]. The solution of the (e.g. potassium) salt thus obtained was then filtered and water was evaporated from the filtrate to yield a purified salt suitable for use directly in an ink as described below.

35

Inks

The effectiveness in ink jet printing of compounds of Formula (1) was demonstrated as follows. Inks separately comprising each exemplified dye were prepared by dissolving 2 parts of the sodium salt, prepared as described above, in 98 parts of a mixture of water and 2-pyrrolidone (in a respective ratio of 90:10 by volume). The inks were printed onto gelatin paper (obtained from Felix Schoeller) using a thermal ink-jet printer to give a bright cyan prints which had excellent light fastness.

Further inks comprising the exemplified dyes may be prepared as described in the following tables in which the number in the first column (headed Ex. no.) denotes the example number of dye to be used in the ink. The dye may be in its free acid form and/or in the form of any IJP-effective salt (e.g. sodium, potassium or ammonium salt). Numbers quoted in the second column onwards refer to the number of parts of the relevant ingredient and all parts are by weight. The inks may be applied to paper by thermal or piezo ink jet printing.

The following abbreviations are used in the tables:

PG = propylene glycol; DEG = diethylene glycol; NMP = N-methyl pyrrolidone;  
 DMK = dimethylketone; NaST = Na stearate IPA = isopropanol;  
 MEOH = methanol; 2P = 2-pyrrolidone; MIBK = methylisobutyl ketone;  
 CET = cetyl ammonium bromide; TBT = tertiary butanol; TDG = thiodiglycol;  
 BDL = butane-2,3-diol; PHO =  $\text{Na}_2\text{HPO}_4$ ; P12 = propane-1,2-diol.  
 CHL = cyclohexanol; and PDL = pentan-1,5-diol.

TABLE I

Ex. no.	Dye	Water	PG	DEG	NMP	DMK	MEOH	2P	MIBK
1	2.0	80	5		6	4		5	
2	10.0	85	3		3	3	5	1	
3	2.1	91		8					1
4	2.4	75	3	4		5	6		5
5	5.1	96					4		
6	1.8	80		5				15	
7	2.6	84			11			5	
8	3.3	80	2			10	2		6
1	5.4	69	2	20	2	1		3	3
2	7.0	70			15		3		10

14

TABLE II

Ex. No.	Dye	Water	PG	DEG	NMP	NaOH	Na ST	IPA	2P	MIBK
3	2.0	70		7		6		3		2
4	4.0	65	4		6		0.7		5	
5	1.0	50		4				5		1
6	3.1	86	5			2	0.2	4		5
7	1.1	81		2	9	0.5	0.5		9	

TABLE III

5

Ex. no.	Dye	Water	PG	DEG	NMP	DMK	IPA	MEOH	2P	MIBK
8	3.1	86	5				4			5
1	1.1	81			9				9	
2	2.5	60	4	15	3	3	6	10	5	4
3	3.2	65		5	4	6	5	4	6	5
4	10.0	80	2	6	2	5	1		4	

TABLE IV

Ex. no.	Dye	Water	PG	DEG	NMP	DMK	NaOH	Na ST	IPA
5	3.0	90		5	5		0.2		
6	5	65	5	20					10
7	4.1	80		5	2	10		0.3	
8	10.8	90	5						5
1	12.0	90				7	0.3		3

10

15

20



15

TABLE V

Ex. no.	Dye	Water	PG	DEG	NMP	CET	PHO	2P	P12
2	3.0	80	15			0.2		5	
3	9.0	90		5			1.2		5
4	2.5	90		6	4		0.12		
5	3.1	82	4	8		0.3			6
6	10.0	91			6			3	
7	5.0	78	5	11				6	
8	6.0	63	3		4		2.0		
1	3.0	72		15		0.8			3
2	5.4	86	5		7		3.0	7	
3	2.0	90		10					10

TABLE VI

5

Ex. no.	Dye	Water	PG	DEG	NMP	CET	TBT	TDG
4	1.5	85	5	5		0.15	5.0	0.2
5	9.0	90		5	5			0.3
6	2.0	90		10				
7	2.0	88						10
8	5.5	70	4		4	0.4	3	

TABLE VII

Ex. no.	Dye	Water	PG	DEG	NMP	TBT	TDG	BDL	PHO	2P
1	0.9	85		10				5	0.2	
2	4.0	70		10	4			1		4
3	2.2	75	4	10	3			2		6
4	9.0	76		9	7	3.0			0.95	5
5	2.1	70	5	5	5	0.2	0.1	5	0.1	5

10

15

TABLE VIII

Ex. no.	Dye	Water	PG	DEG	NMP	TBT	TDG	2P
6	3.0	55			5	2.0		3
7	6.0	65		4		0.1	5	
8	5.0	78			5		12	5
1	8.0	70	2		8		15	5
2	10.0	80					8	12

TABLE IX

Ex. no.	Dye	Water	PG	DEG	NMP	BDL	PHO	2P	P12
3	10.0	75	3		5	3		3	1
4	3.5	80		6					5
5	2.0	90	7			7	0.5		
6	6.0	65			5			2	
7	4.0	70		10	4	1		4	11

TABLE X

Ex. no.	Dye	Water	PG	DEG	NMP	CET	TBT	TDG	BDL	PHO	2P
8	1.5	80	1	2	3	0.5	0.4		7	2	10
1	3.0	60		4		2.0		0.5			
2	4.5	90		3	6		7.0		1	3	2
3	3.0	95		7		4		3		0.5	
4	2.1	70	5	5	5	0.1	0.2	0.1	5	0.1	5

TABLE XI

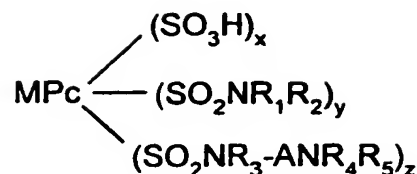
Ex. no.	Dye	Water	PG	DEG	NMP	CHL	PHO	2P	PDL
5	7.0	75	3		5	3		3	1
6	3.5	60			2				5
7	2.0	90	7			7	1.5		2
8	6.0	65			5			2	
1	4.0	70		5	4	1		4	12

5

10

CLAIMS

1. A compound of Formula (1):

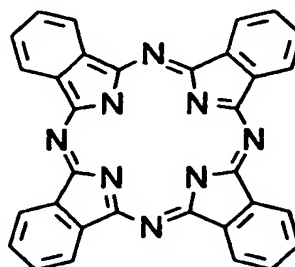


Formula (1)

which includes all IJP-effective forms of such compounds; and in which

M represents a metal or H;

Pc represents a phthalocyanine nucleus of Formula (2)



$x + y + z$  represents an average from 3 to 4; and  $z$  may be zero.

A represents  $\text{C}_{1-4}$ -alkylene;

$\text{R}_1$ ,  $\text{R}_3$  each independently represent H or  $\text{C}_{1-4}$ -alkyl;

$\text{R}_4$  represents H; or  $\text{C}_{1-4}$ -alkyl optionally substituted with hydroxy;

$\text{R}_5$  represents a carboxylic acid substituted aryl group; and

$\text{R}_2$  represents H,  $\text{C}_{1-4}$ -alkyl or a group of formula BD

where

B represents  $\text{C}_{1-4}$ -alkylene; and

D represents  $\text{NR}_6\text{R}_7$ ; or  $\text{SC}_{1-4}\text{alkyleneSO}_3\text{H}$ ;

where

$\text{R}_6$  represents H; or  $\text{C}_{1-4}$ alkyl, optionally substituted by hydroxy;

$\text{R}_7$  represents H;  $\text{C}_{1-4}$ alkyl, optionally substituted by hydroxy or morpholino;

or  $\text{R}_6$  and  $\text{R}_7$  together with the N atom to which they are attached form a morpholino or piperazino ring.

2. An ink effective for use in ink jet printing, comprising a medium and a colorant comprising an IJP-effective compound of Formula (1) as claimed in claim 1.

3. A process for printing a substrate with an ink as claimed in claim 2, using an ink-jet printer.
- 5 4. A substrate printed with an ink as claimed in claim 2, the substrate selected from one or more of: paper, an overhead projector slide and a textile material.
5. A process for the colouring a textile material with an ink as claimed in claim 2, the process comprising the steps of:
- 10 i) applying the ink to the textile material by ink-jet printing; and  
ii) heating the textile material at a suitable temperature to fix the ink on the material.
6. A textile material coloured with an ink as claimed in claim 2.
- 15 7. A process for preparing a dye of Formula (1) as claimed in claim 1, the process comprising the steps of:
- i) condensing the compound of formula  $\text{MPc}(\text{SO}_2\text{Cl})_{x+y+z}$  with a halo amine of formula  $\text{NHR}_3\text{AX}$ , where X is halo;
- ii) treating the halogenated adduct from step i) with a base, optionally ammonium hydroxide; and
- 20 iii) reacting the material from step ii) with an amine of formula  $\text{NHR}_4\text{R}_5$  to produce a dye of Formula (1);
- where x, y, z, M, Pc, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub> and A are as represented in claim 1.

# INTERNATIONAL SEARCH REPORT

Int. Application No  
PCT/GB 98/01015

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C09B47/26 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C09B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 596 383 A (BAYER AG) 11 May 1994 see the whole document ---	1-7
X	WO 97 13814 A (ZENECA LTD ; MISTRY PRAHALAD MANIBHAI (GB); KENYON RONALD WYNFORD ( ) 17 April 1997 see abstract; examples ---	1-7
Y	PATENT ABSTRACTS OF JAPAN vol. 013, no. 372 (C-627), 17 August 1989 & JP 01 126381 A (RICOH CO LTD), 18 May 1989, see abstract --- -/-	1-7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"S" document member of the same patent family

Date of the actual completion of the international search

26 June 1998

Date of mailing of the international search report

09/07/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Dauksch, H

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 98/01015

(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 97 13811 A (ZENECA LTD ;MISTRY PRAHALAD MANIBHAI (GB); KENYON RONALD WYNFORD ( ) 17 April 1997 see abstract see page 3, line 9 - page 4, line 9 ----	1-7
Y	EP 0 468 649 A (ICI PLC) 29 January 1992 see example 1 ----	1-7
A	EP 0 519 395 A (EASTMAN KODAK CO) 23 December 1992 see abstract; example 98 ----	1-7
A	FR 2 033 597 A (UGINE KUHLMANN) 4 December 1970 see page 1, line 10 - page 2, line 17 ----	1-7
A	US 4 033 980 A (MEININGER FRITZ ET AL) 5 July 1977 see the whole document ----	1-7
A	DE 28 12 261 A (CIBA GEIGY AG) 28 September 1978 see page 40, last paragraph - page 41, paragraph 1 -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. .dional Application No

PCT/GB 98/01015

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0596383 A	11-05-1994	DE 4237545 A	11-05-1994
		DE 59308069 D	05-03-1998
		JP 2655804 B	24-09-1997
		JP 7331106 A	19-12-1995
		US 5489330 A	06-02-1996
WO 9713814 A	17-04-1997	AU 6993896 A	30-04-1997
WO 9713811 A	17-04-1997	AU 6993596 A	30-04-1997
EP 0468649 A	29-01-1992	AT 138088 T	15-06-1996
		AU 642270 B	14-10-1993
		AU 8017391 A	30-01-1992
		DE 69119499 D	20-06-1996
		DE 69119499 T	19-09-1996
		ES 2086488 T	01-07-1996
		JP 4270286 A	25-09-1992
		US 5189154 A	23-02-1993
EP 0519395 A	23-12-1992	US 5248538 A	28-09-1993
		CA 2070347 A	19-12-1992
		DE 69223089 D	18-12-1997
		DE 69223089 T	10-06-1998
		JP 5185735 A	27-07-1993
FR 2033597 A	04-12-1970	NONE	
US 4033980 A	05-07-1977	DE 1795140 A	02-03-1972
		BE 737593 A	18-02-1970
		CA 918657 A	09-01-1973
		CH 551478 A	15-07-1974
		FR 2015822 A	30-04-1970
		GB 1285466 A	16-08-1972
DE 2812261 A	28-09-1978	CH 640238 A	30-12-1983
		AT 361637 B	25-03-1981
		AU 3475778 A	11-10-1979
		BE 865291 A	25-09-1978
		BR 7801778 A	19-12-1978
		BR 7801806 A	02-01-1979

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/01015

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 2812261 A		CA 1138442 A	28-12-1982
		CS 222257 B	24-06-1983
		DD 137058 A	15-08-1979
		EG 13483 A	30-06-1981
		FR 2387658 A	17-11-1978
		FR 2387985 A	17-11-1978
		GB 1593623 A	22-07-1981
		GB 1593624 A	22-07-1981
		HK 44284 A	25-05-1984
		IN 148123 A	25-10-1980
		JP 1705632 C	27-10-1992
		JP 3071401 B	13-11-1991
		JP 53119884 A	19-10-1978
		JP 1808368 C	10-12-1993
		JP 2000181 A	05-01-1990
		JP 5015714 B	02-03-1993
		JP 1279807 A	10-11-1989
		JP 1787057 C	10-09-1993
		JP 4077040 B	07-12-1992
		KE 3381 A	23-03-1984
		NL 7803095 A	27-09-1978
		US 4318883 A	09-03-1982
		US 4530924 A	23-07-1985
		ZA 7801708 A	28-03-1979



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☒ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**